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# Metal fluxes in the Mersey Narrows

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## Abstract

Surveys of the Mersey estuary in north-west England were undertaken near the mouth of the estuary in the region known as the Mersey Narrows. Tidal fluxes of suspended and dissolved matter, particularly heavy metals, through the Mersey Narrows were investigated. This paper gives results of conducting four intensive cross-sectional surveys of the Narrows, during which currents, salinities, turbidity and water samples were obtained systematically at numerous positions, throughout selected tidal cycles. Over 300 water samples per survey were analysed to yield suspended and dissolved concentrations of the elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, at all states of the tide. Suspended solids, concentrations and salinities were also measured. Suspended particulates account for the majority of each element present, except for cadmium, which was present in roughly equal dissolved and suspended fractions. From the tidal current and water quality data, calculations were made of hour-by-hour fluxes of each component, to show the detailed ebb and flow of heavy metals and the net tidal transport of each component. Although some differences between landward transport on the flood tide and seaward transport on the ebb were not significant, the more definite results consistently showed a seawards net transport. For spring tides of high tidal range, there was an indication of an opposite tendency, reducing the seawards transport or even reversing it, for certain suspended components.

**Keywords:** Mersey estuary, surveys, tidal flux, dissolved metals, particulate metals, salinity, suspended particulate matter, suspended solids

## Introduction

### MOTIVES AND SCOPE OF THE 1982-88 SURVEYS

Because of their impact on coastal fish populations and on the health of those who eat fish caught in coastal seas, the quantities of heavy metals entering coastal waters is of concern. An awareness of the need to quantify such inputs was heightened in the late 1970s with the implementation of the Dangerous Substances Directive (Council of European Communities 1976). It had long been recognised that the major source of inputs is from man-made sources entering rivers and going out to sea via estuaries. However, the quantities of metals transported are not well known.

Recognising the potential impact of the COPA II legislation (Control of Pollution Act 1974 Part II) on the discharge of effluents and sludges to the Mersey estuary and nearby coastal areas in north-west England, discussions were held in 1981 between North West Water Authority and WRc with a view to pursuing a collaborative study with the two objectives:

- To determine the fluxes in suspension and solution of eight trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb and

Zn) through the Mersey Narrows during selected tidal cycles.

- To relate the knowledge so gained to the composition of bottom deposits and to tidal scour in order to assess the efflux or influx of metals pollution.

Prior to this study, little was known about the vertical, lateral and temporal concentration gradients of these elements in the Mersey. This information is necessary to quantify their transports into and out of the estuary. Four surveys were, therefore, planned at a well-defined cross-section near the mouth of the estuary (Fig. 1), each covering a full-tidal cycle. This work was planned by the authors, in consultation with National Rivers Authority and North West Water Authority staff, and it attracted the financial support of the Department of the Environment over a six year period, from April 1982 to March 1988, proceeding in two phases.

Phase 1 spanned 1982-1985 and was devoted largely to the measurement of tidal transport of the eight elements of interest, during four different tidal cycles, of diverse tidal

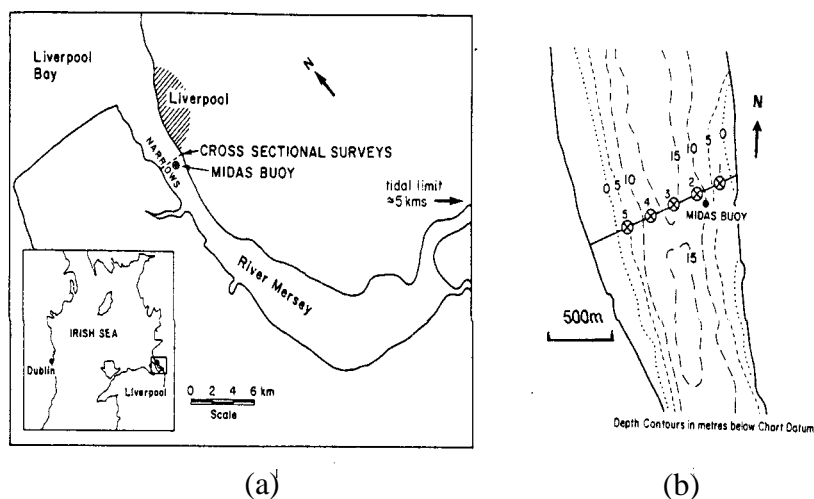


Fig. 1. Location of cross-sectional surveys in the Mersey Narrows; (a) general location; (b) detail of the surveyed section

range. Both the dissolved and the suspended particulate matter were sampled. These results and their interpretation form the scope of this paper.

It is intended that further papers will describe other Phase 1 work in which sediment cores from throughout the estuary were sampled and analysed. This included an exercise carried out in June and August 1982, tracing the dispersal of radio-labelled silt.

Phase 2 of the study, in 1985-1988, set up a long-term monitoring station called MIDAS, which was established near the original survey section 13, as described in Prandle *et al.* (1990). Meanwhile, considerable statistical and computational effort both at WRc and at the Proudman Oceanographic Laboratory, Bidston, went into verifying that measurements at the MIDAS anchorage, of turbidity, salinity and current velocity at two depths in the water column, would be representative of matter transported through the full width of the estuary. In their analysis of the tidal constituents of water and sediment transport in the Mersey, Prandle *et al.* (1990) made particular use of a practically-continuous three-month data set (3 April to 3 July 1986) of current speed and direction, measured by MIDAS at 15-minute intervals.

The interval of 15 years between the tidal-cycle surveys of eight metal constituents (which were reported to the Department of the Environment, to the National Rivers Authority and to North West Water in 1986), and publication of this paper now is regrettable, but has not been imposed by commercial or other confidentiality. Both authors were engaged on the Mersey Metals Flux Study throughout the 1980s but have had to wait for the opportunity, in retirement from WRc plc, to publish the results more widely.

## RELATED STUDIES

Up until the time of writing no such cross-sectional study of estuarine metals fluxes has been made, before or since the work reported here, either in the Mersey Estuary or any other British estuary. However work in the tidal Elbe, Germany, by Michaelis (1983a, b, 1991) and colleagues at GKSS, Geesthacht, is closely akin to the Mersey Metals Flux study. These workers studied the tidal reaches around the port of Hamburg, with cross-sectional sampling and moving-boat velocity measurements, to evaluate Fe, Ni, Pb, As, Sb, Hg, and Mn transport in the water and 15 elements in the suspended sediment of the Elbe River. Mention should also be made of Klinkhammer and Bender (1981) who obtained a mass balance of inputs and outputs of Fe, Ni, Cu, Mn, Zn and Cd in the Hudson Estuary, USA, based largely on mid-channel measurements.

Previous studies on the Mersey Estuary focused largely on its discharge, salinity, sediment transport and mixing processes (e.g. Bowden, 1960; Bowden and Sharaf el Din, 1966; Bowden and Gilligan, 1971; Halliwell and O'Connor, 1975). Assessments have been made of the annual inputs of metals and other pollutants into the North Sea (Norton, 1982) and into the Irish Sea (Head, 1985). The distribution of Hg in the Mersey Estuary sediments has been described by Campbell *et al.* (1986) and that of various trace metals in solution and suspension in the Mersey Estuary has been reported by Campbell and Riley (1984).

Hydrometric work has continued in the Mersey Narrows by the National Rivers Authority, in association with the Proudman Oceanographic Laboratory (POL), using acoustic Doppler current profilers to gain a better understanding of the tidal currents and hence of the water fluxes (Lane *et al.*,

1997). The earlier paper by POL workers (Prandle *et al.*, 1990) reviewed flux measurement procedures for the River Mersey, focusing on water and salinity movements, including some of the data from the above-mentioned cross-sectional surveys.

Other than the above, the closest subsequent comparison to the original 1982-85 Mersey Metals Flux surveys is seen in the Humber Estuary. Many projects in that estuary have been tackled under the auspices of the U.K. Land-Ocean Interaction Study (LOIS), as described by Wilkinson *et al.* (1997) and in an Editorial of the Marine Pollution Bulletin (1998). LOIS projects on the Humber have included:

- Load estimation methodologies for British rivers (Webb *et al.*, 1997).
- Monitoring of turbidity, interpreted with the aid of remote-sensed imagery, for suspended sediment transport in the Humber catchment (Wass *et al.*, 1997).
- Fluxes of the Humber's suspended sediments and salinity (Uncles *et al.*, 1998; Wu *et al.*, 1998)
- Estimating Humber sediment fluxes with the help of airborne images (Brown *et al.*, 1998; Robinson *et al.*, 1998)

From the above broad spread of work, the studies closest to the Mersey Metals Flux work are those of Wu *et al.* (1998) who made half-hourly observations in June 1985 of current speed and direction, temperature, conductivity, salinity and light transmission over a tidal cycle, at 1 m or 2 m depth intervals through the water column, from an anchored boat station. The boat station was moved across the estuary mouth to a different site each day of the survey.

The work of Robinson *et al.* (1998) also resembles the Mersey Metals Flux project, in sampling across the Humber estuary mouth, using five anchored boat stations, but their sampling was restricted to the top 0.2 m of water during a single spring tide (10 August 1995). The five-station sampling was complemented by aerial observations of turbidity. With various assumptions regarding the depth-variation of suspended solids, an estimate could be made for the flux of suspended solids through the whole cross-section of the estuary mouth.

In none of the above Humber LOIS studies has the heavy metal content been observed, in either the dissolved or suspended form, as was done in the work in the Mersey Narrows.

Jones (2000) has described how the Mersey Estuary has improved in water quality over the past 12 years, as a consequence of improved sewage treatment and industrial wastewater treatment inland. There has been a dramatic reduction in some of the metals inputs to the estuary,

particularly that of Hg discharged from chlor-alkali plants; consequently the surveys reported here were observing larger fluxes of heavy metals than would be found today. Thus, despite the inherent uncertainties in flux estimates, the 1982-84 tidal surveys probably present as clear a picture as will ever be possible of the temporal and spatial flux variation in the Mersey Narrows.

## Location of tidal surveys

A cross-section near the mouth of the Mersey (Fig. 1) was chosen for detailed study. The choice was based on the need for a key site where the movements of material both into and out of the estuary could be assessed. The Mersey Narrows were chosen because:

- (1) the Narrows possess a well-defined cross-section;
- (2) there is little or no sediment on the bed at this location which makes quantification of the transport of material an easier task.

Four tidal cycle surveys were completed during the period 1982-84. The details of the timings of the surveys are listed in Table 1 together with their tidal characteristics and the freshwater discharge to the estuary on each occasion. The weather and sea state during each of the four surveys were good. To work mostly in daylight, the 16 June 1982 survey went from peak-to-peak of the flood tide: all the other surveys went from the lowest ebb-to-ebb times. These surveys provided a range of environmental conditions.

- 16 September 1982 was near the equinox and thus furnished one of the largest spring tides of the year, in conjunction with a rather small freshwater discharge.
- This contrasts with the 21 September 1983 spring tide with freshwater discharge about nine times as great.
- The 16 June 1982 event was a neap tide of low tidal range near the solstice.
- The other example was intermediate in tidal range and freshwater flow.

## Methods

### SURVEY METHODS

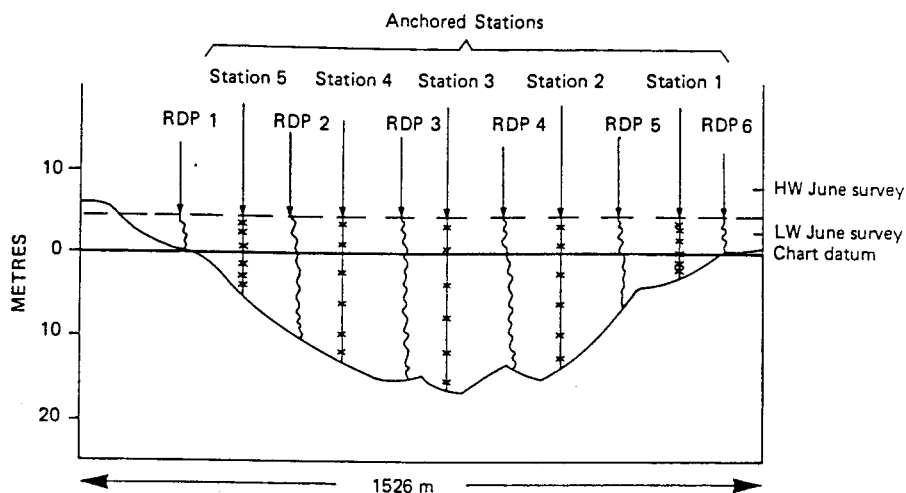
Table 2 and Figs. 2 and 3 summarise the methods used during each of the four surveys. Five boat stations spaced at regular intervals across the estuary at the survey section were used on all surveys except that of 21 Sept. 1983 in which four stations only were used. The boats were each held to their station with a single bow anchor; thus at the turn of the tide the boats would swing around to face the oncoming current. This movement was carefully monitored from the shore. The

*Table 1.* Measured times and heights of tides at Prince's Pier tide gauge and freshwater input to the estuary for the four surveys

		<i>High and low water-times and heights</i>			<i>Freshwater input (m<sup>3</sup> s<sup>-1</sup>)</i>
	<i>Measured Time (GMT)</i>	<i>Height<sup>(1)</sup> (m)</i>	<i>Tidal range Measured (m)</i>	<i>Mean (m)</i>	
16 June 1982	0550	8.00			
	1235	2.39	5.61		
			5.18	5.35	40
	1835	7.57			
16 Sept 1982	0442 <sup>(2)</sup>	1.02 <sup>(2)</sup>			
	1020	9.22	8.20		
			8.07	8.14	10
	1650	1.15			
21 Sept 1983	0510	1.54			
	1050	8.80	7.26		
			7.18	7.22	87.5
	1710	1.62			
9 Aug 1984	0355	2.00			
			5.97		
	0955	7.97	6.05		
			6.48	6.17	8.28
	1615	1.92			
	2205	8.40			

(1) Height relative to Chart Datum. Second decimal place estimated by eye from chart-recording for measured values.

(2) From Tranmere tide gauge as Prince's Pier gauge inoperative at the time.



*Fig. 2.* Cross-section of Mersey Narrows at Section 13, showing current metering points (x) and RDP positions.

Table 2. Mersey surveys 1982-84

	<i>Survey A</i> <i>16 June 1982</i>	<i>Survey B</i> <i>16 Sept 1982</i>	<i>Survey C</i> <i>21 Sept 1983</i>	<i>Survey D</i> <i>09 Aug 1984</i>
No. of Stations	5	5	4	5
Rapid Drop* Profiling	Transverse; at survey section	Along axis of the Narrows	Transverse; at survey	V.intensive transverse; at survey section**
Position fixing***	Sextant	Sextant	Laser range finder	Laser range finder
Longitudinal surface sampling	Yes	Yes	Yes	Yes

+ Vertical continuous profiles of turbidity and salinity

\*\* Included collection of additional water samples at each station at each of three depths for suspended solids analysis and size-fractionation

\*\*\* Of both RDP vessel for each station and for each of the anchored stations at regular intervals

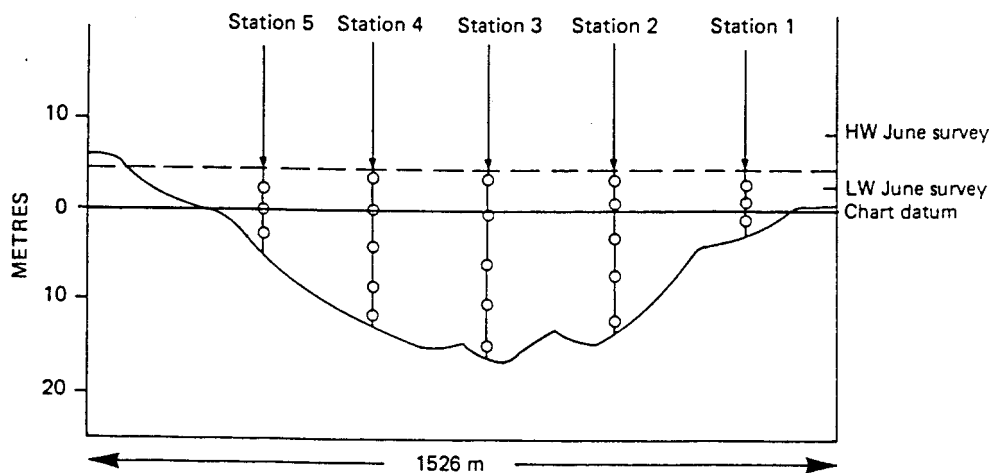


Fig. 3. Cross-section of Mersey Narrows at Section 13 showing sampling points (o)

boats were on charter hire from local firms, with professional masters and crew. The water quality sampling was done by two or three WRC and NWWA staff on board each vessel; the current metering and drop profiling work was carried out by Hydraulics Research staff.

At each station throughout a tidal cycle, water samples were collected hourly (from five different depths at stations

2, 3 and 4 and three different depths at stations 1 and 5; see Fig.3). The water samples were transferred by NWWA inflatable dinghy every three or four hours to a shore laboratory for filtration and preservation. Current velocity measurements were made half-hourly using a directional current meter at six different depths (Fig.2). The current meter utilised (i) a Braystoke 001 impeller actuating a reed switch

(ii) a Druck PDCR pressure transducer for depth measurements and (iii) a fluxgate compass.

To gain information between the anchored stations, continuous profiles of turbidity and salinity were obtained using a Rapid Drop Profiler (RDP) supplied and operated by Hydraulics Research Ltd. (Fig. 2). The scope of this technique was extended during the 1984 survey to include the collection of water samples from three different depths at every RDP station. These samples were analysed for suspended solids concentration and yield a more accurate picture of the distribution between the anchored stations. The major difficulty encountered during the surveys was station-keeping by vessels located at stations 2, 3 and 4. The holding ground in the Narrows is poor and consequently, anchor drag in the prevailing strong currents was a problem. Although accurate position-fixing at regular intervals, together with the avoidance of sampling whilst the position of the vessel was changing, it was subsequently shown that this aspect of the study was the largest contributor to the total error in a net tidal transport determination.

#### TREATMENT OF SEAWATER SAMPLES

Filtration, sub-sampling and preservation of tidal survey samples for subsequent analysis was not performed on board the vessels because of the danger of contamination. Instead, samples were transferred to a laboratory at the University of Liverpool where it was possible to treat the majority of the samples during the day of the survey. On occasions when it was not possible to complete treatment of all 300 samples during that day, then a selected few were put aside to await treatment the following day. Sample stability tests with respect to storage have been described by Campbell *et al.* (1985). The subsequent metals analysis was mostly carried out at WRc. But Cr and certain Hg determinations were carried out by the Department of Oceanography, University of Liverpool. The analytical performance is described below.

#### CHEMICAL ANALYSIS

The analytical methods used are summarised in Fig.4. The procedure shown for indirect estimation of particulate As from total and dissolved data was used on both 1982 surveys.

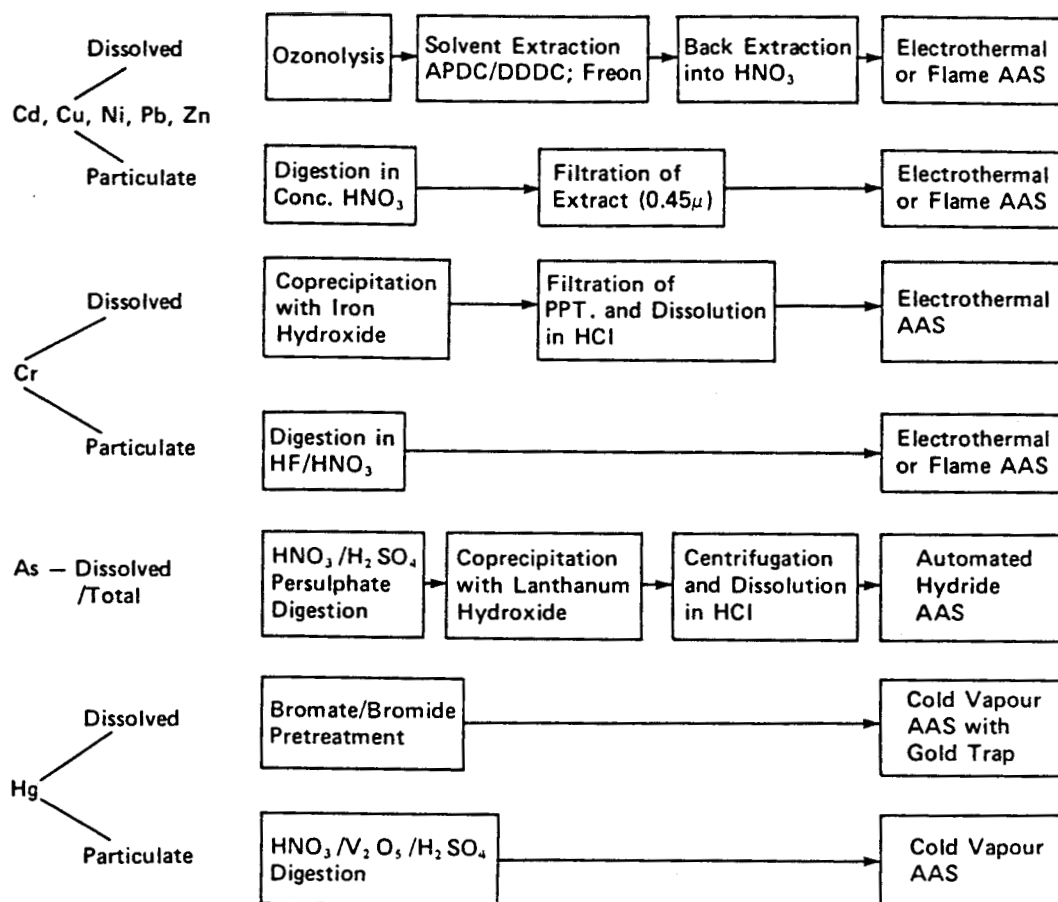


Fig. 4. Analytical methods

However, on the 1983 and 1984 surveys direct measurement was performed through acid digestion of samples collected on 0.45 mm membrane filters.

#### ANALYTICAL PERFORMANCE — DISSOLVED METALS

The Limits of Detection (LOD) achieved are listed in Table 3. For the majority of elements these were adequate for determination of typical levels found on the surveys, although a somewhat lower LOD would have been desirable in the case of Pb. To check that analytical results were free of contamination during handling of samples and subsamples, deionised water blanks were inserted randomly amongst the estuary samples and subjected to the same preservation, storage, filtration and analysis routine. Standard deviations for these blanks were generally within the range of the LOD previously established, as shown in Table 3. Unfortunately, for the 1982 surveys, all dissolved Hg results were vitiated by severe contamination problems. These problems were overcome in later surveys, by change of preservative and by changing from a 142 mm PTFE/stainless steel filter unit to a 47 mm polycarbonate unit. Percentage relative standard deviation (r.s.d) estimates for the methods used are also shown in Table 3. Such information is of particular interest since a knowledge of the precision of metal concentration measurements is an important factor in the assessment of errors in the determination of net tidal fluxes. For Cd, Cu, Ni, Pb and Zn the r.s.d. estimates were obtained from control charts prepared during routine analysis using a sample of filtered Mersey estuary water. However, for As and Cr only

within-batch estimates for spiked sea (As) or estuary (Cr) waters were available.

#### ANALYTICAL PERFORMANCE — PARTICULATE METALS

Particulate phase performance data are shown in Table 4. Percentage r.s.d. estimates for Cd, Cu, Ni, Pb and Zn were obtained from routine quality control charts, as for the dissolved phase, while those for As, Cr and Hg are within-

Table 4. Limits of detection, precision and standard deviation of blanks for particulate phase analysis

Typical survey concentration range (mg l <sup>-1</sup> )	Precision (relative standard deviation)	Limits of detection (mg l <sup>-1</sup> )	Std deviation of blanks (mg l <sup>-1</sup> )	
			June 1982	Sept 1982
As 0-60	8%	0.7	0.14	0.17
Cd 0-5	7%	0.007	0.009	0.002
Cr 0-250	6%	*	0.40	0.08
Cu 0-400	9%	0.3	8.0	0.15
Ni 0-200	7%	0.3	0.35	0.23
Pb 0-500	7%	0.2	0.33	0.04
Zn 0-1500	6%	0.7+	5.7	2.4
Hg 0-6	4%	0.04	0.020	0.031

+ Quoted LOD does not take account of filter blank variability

\* data not available

Table 3. Limits of detection, precision and standard deviation of blanks for dissolved phase analysis

Typical survey concentration range (mg l <sup>-1</sup> )	Precision (relative std deviation, percentage)	Limits of detection (mg l <sup>-1</sup> )	Std deviation of blanks (mg l <sup>-1</sup> )			
			June 1982	Sept 1982	Sept 1983	Aug 1984
As 2-10	8	0.7	0.14	0.42	*	*
Cd 0.1-0.5	10	0.03	0.024	0.013	0.005	0.008
Cr 0.1-2.0	4	0.03	0.047	0.060	0.030	*
Cu 2-8	6	0.6	0.33	0.21	0.21	0.13
Ni 1-11	4	0.5	0.05	0.11	0.08	0.05
Pb 0.5-7	21	0.6	0.12	0.44	0.16	0.10
Zn 10-50	4	2.6	0.50	0.49	0.71	0.79
Hg 0.01-0.08*		<0.001	*	*	*	*

\* data not available



batch estimates from method testing. The Limits of Detection achieved were sufficiently low for them to be applicable to the vast majority of the samples analysed, with the exception of some from the June 1982 neap tide survey which had extremely low suspended matter loadings. Very high Cu and Zn field blanks (from reagents and deionised water in lieu of sample) were found on this survey but after modification of the Millipore 142 mm filter units a dramatic improvement was achieved for Cu on the September 1982 survey. The fact that the Zn blanks were still somewhat higher and more variable than desirable can be accounted for by the Zn content of the membrane filters themselves and this was one of the reasons for opting for smaller 47 mm filters on the 1983 and 1984 surveys. Blank tests for the particulate samples were not performed for the latter surveys but the approximately ten-fold reduction in filter weight would be expected to have resulted in a substantial improvement.

#### CALCULATION OF HALF-TIDAL AND NET TRANSPORTS

Linear interpolation between current metering or sampling points was used to assign values for velocity and concentration at each point in a dense three-dimensional grid (lateral position, depth, time) which encompassed the cross-section. The flux through each element of cross-sectional area was derived from the individual elements of velocity times concentration. The elementary fluxes were then integrated over the cross-section and through time to give the net tidal transport. The numerical methods employed have been described by Marsh (1983).

The tides impose an oscillating transfer of large volumes of water into and out of the estuary, with its own load of dissolved and suspended matter. The net tidal transport is the relatively small difference between the amounts

transported on the flood and ebb tides, i.e. between two large and opposing movements. The relative size of these two terms varies from tide to tide and the definition of tidal cycle is crucial to the results obtained. To facilitate comparison between transports measured on different surveys, this study defines a tidal cycle length based on the transport of water in which the oscillating flood and ebb components are forced to be equal in volume and the net transport of water over the period is equal to the freshwater discharge to the estuary over that period. The calculation of the error associated with a net tidal transport has been detailed elsewhere (Marsh, 1983; Potter, 1985) and is exemplified below.

## Results and discussion

### TRANSPORT OF SALT AND WATER DURING THE MERSEY FLUX STUDIES

Table 5 demonstrates that the freshwater flow was small compared to the tidal flow. For example, the ratio of ebb-tide water transport to freshwater transport during the 6.17 m survey was  $254.98/(0.5 \times 0.39) = 1307$  to 1 over the ebb half-cycle; at the other extreme, for the 7.22 m survey, which experienced the greatest freshwater flow of the four surveys, the corresponding ratio was 172 to 1. Table 6 shows the effect of the chosen tidal cycle definition (based on a net water transport equal to the freshwater input to the estuary) upon the salt balance. In all four surveys the net mass transport of salt in the tidal cycle was less than  $\pm 0.06 \times 10^6$  tonnes.

### TRANSPORT OF SUSPENDED SOLIDS

The variation of suspended solids transport with tidal range is shown in Table 7. The half-tide transport increased as the tidal range increased: from 6069 tonnes on a 5.35 m tide to

Table 5. Water transport

Mean tidal range (m)	10 <sup>6</sup> m <sup>3</sup>			(%)	
	Net tidal*	Flood (-)	Ebb (+)	Net/Flood	Net/Ebb
5.35	1.74	212.37	214.11	0.8	0.8
6.17	0.39	254.59	254.98	0.2	0.2
7.22	3.42	270.05	273.47	1.3	1.3
7.22	3.42	270.05	294.32	0.1	0.1

Table 6. Salt transport

Mean tidal range (m)	10 <sup>6</sup> tonnes			(%)	
	Net tidal*	Flood (-)	Ebb (+)	Net/Flood	Net/Ebb
5.35	0.018	6.236	6.254	0.3	0.3
6.17	0.007	7.673	7.680	0.1	0.1
7.22	0.043	7.834	7.877	0.6	0.6
8.14	-0.058	8.852	8.794	0.7	0.7

\* Tidal cycle defined as that period of time during which the net transport of water is equal to the freshwater input to the estuary. Transport seawards is positive; landwards is negative.

Table 7. Suspended solids transport

Mean tidal range (m)	tonnes			(%)	
	Net tidal*	Flood (-)	Ebb (+)	Net/Flood	Net/Ebb
5.35	837	6069	6906	13.8	12.1
6.17	-423	25852	25429	1.6	1.7
7.22	-889	56472	55583	1.6	1.6
8.14	-788	59091	58304	1.3	1.4

\* Tidal cycle defined as that period of time during which the net transport of water is equal to the freshwater input to the estuary. Transport seawards is positive; landwards is negative.

59091 tonnes on an 8.14 m tide. It is of interest that the transport more than doubled in going from a 6.17 m tide to a 7.22 m tide, whereas there was little change between a 7.22 m and an 8.14 m tide. However, the change in going from a 5.35 m tide to a 6.17 m tide was even more dramatic, there being a four-fold increase in the suspended solids transport. It is thought that the 5.35 m tide on this occasion was rather exceptional in that the observed suspended solids concentrations were lower than normal. The net tidal transport of suspended solids during the 5.35 m tide was unique among the four surveys in that its direction was seawards. However, when the net tidal transport was compared to the half-tide transport, only the 5.35 m tide showed a conspicuous net transport in percentage terms. It is also of interest to note that the net tidal transports in all four surveys were similar in absolute magnitude although the half-tide transports varied by a factor of ten over the tidal range considered.

#### TRANSPORT OF METALS: DISSOLVED, PARTICULATE AND TOTAL

The concentrations of eight heavy metal elements, namely As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were determined in each water sample. With a few exceptions the concentration of each element was measured separately in the dissolved (d) and particulate (p) fractions, their sum yielding the Total (t). The d,p,t notation is used in the discussion below.

#### Dominant modes of transport

Table 8 shows the transport in kilograms of each element

for each of the four surveys, for the Flood Tide bringing material into the estuary, and for the Ebb Tide transporting material out to sea. The Net Tidal columns give the difference between the Ebb and Flood transports, positive values denoting a seawards net transport.

The particulate phase was the dominant mode of transport for Cr, Pb and Hg. It was also the more important mode for Zn during spring tides. The dissolved phase became the more important mode for As, Cd and Ni during the 5.35 m tide, probably as a consequence of the extremely low suspended solids load. Both the dissolved and particulate phases were important modes of transport for these three elements during the other three surveys, as was the case for Zn during the 5.35 m tide. The contrasting behaviour of dissolved and particulate Ni and Zn is discussed in more detail in Campbell *et al.* (1988).

Contamination of samples prevented results being obtained for Hg(d) in two cases and for Cu(p) in one case. In addition, it was shown that Cu samples are unstable with respect to suspended particulate matter - water exchange and, therefore, results for this metal are discussed below only with reference to total metal.

Zn is the dominant metal in the tidal movements at the surveyed section, with over 30,000 kg (>30 tonnes) moving on the spring tides, mostly as the particulate fraction. Of the other metals, Pb, Cu and Cr have movements about a quarter of that of Zn; and As and Ni of the order of one tenth of that for Zn. The few tens or hundreds of kilograms assessed for Cd and Hg are far from insignificant, in terms of their pollution potential. Note that Cd is split evenly between the dissolved and particulate phases, which is typical of its behaviour in saline waters.

#### Magnitude of transport

Flood and ebb transports of all elements in the particulate phase increased as the tidal range increased because of the greater suspended solids loads associated with the larger tides. However, the relationships between the dissolved phase transport and tidal range were less distinct: little change was observed between tides in the cases of Ni and Cd; dissolved Zn transport increased with increase in tidal range; the transports of Pb, Cr and As in the dissolved phase varied in an irregular way with change in tidal range, the largest transports of dissolved Cr and As being during the 6.17 m tide, whilst that of Pb was during the 5.35 m tide.

#### Direction of transport

Taking the criterion that net tidal transport is significant if it is greater than 10% of the half-tidal value, the directions of the significant net tidal transports are shown in Table 9. The direction of net transport of total element in all cases except

Table 8. Metal transports - effect of tidal range and distribution between dissolved and particulate phases.

		<i>Mean tidal range (m)</i>																			
		5.35					6.17					7.22					8.14				
		<i>TRANSPORT</i>					<i>TRANSPORT</i>					<i>TRANSPORT</i>					<i>TRANSPORT</i>				
		(kg)		(%)			(kg)		(%)			(kg)		(%)			(kg)		(%)		
		<i>Net<sup>(1)</sup></i>	<i>Flood</i>	<i>Ebb</i>	<i>Net/</i>	<i>Net/</i>	<i>Net</i>	<i>Flood</i>	<i>Ebb</i>	<i>Net/</i>	<i>Net/</i>	<i>Net</i>	<i>Flood</i>	<i>Ebb</i>	<i>Net/</i>	<i>Net/</i>	<i>Net</i>	<i>Flood</i>	<i>Ebb</i>	<i>Net/</i>	<i>Net/</i>
		<i>tidal</i>	<i>(-)</i>	<i>(+)</i>	<i>Flood</i>	<i>Ebb</i>	<i>tidal</i>	<i>(-)</i>	<i>(+)</i>	<i>Flood</i>	<i>Ebb</i>	<i>tidal</i>	<i>(-)</i>	<i>(+)</i>	<i>Flood</i>	<i>Ebb</i>	<i>tidal</i>	<i>(-)</i>	<i>(+)</i>	<i>Flood</i>	<i>Ebb</i>
Ni	d 31		804	835	3.9	3.7	37	882	919	4.2	4.0	91	649	740	14.0	12.3	69	827	896	8.3	7.7
	p 98		259	367	37.8	27.5	105	837	943	12.6	11.1	-191	1822	1631	10.5	11.	-149	2041	1892	73	7.9
	t 1291		1063	1192	12.1	10.8	142	1719	1862	8.3	7.6	-100	2471	2371	4.1	4.2	-80	2868	2788	2.8	2.9
Pb	d 69		612	681	11.3	10.1	13.2	275	408	48.0	32.4	54	305	359	17.7	15.0	40	534	574	7.5	7.0
	p 402		1264	1666	31.8	24.1	133	2232	2365	6.0	5.6	292	7722	8014	3.8	3.6	-717	9501	8784	7.6	8.2
	t 471		1876	2347	25.1	20.1	265	2507	2773	10.6	9.6	346	8027	8373	4.3	4.1	-677	10035	9358	6.8	7.2
Zn	d 426		4640	5066	9.2	8.4	56	5727	5783	1.0	1.0	426	6064	6490	7.0	6.6	407	7074	7481	5.8	5.4
	p 1096		3751	4847	29.2	22.6	1550	10271	11821	15.1	13.1	610	23215	23825	2.6	2.6	-1548	28854	27306	5.4	5.7
	t 1522		8391	9913	18.1	15.4	1606	15998	17604	10.0	9.1	1036	29279	30315	3.5	3.4	-1141	35928	34787	3.2	3.3
Cd	d 6		41	47	14.6	12.8	14	34	48	41.2	29.2	12	35	47	34.3	26.5	0	50	50	0	0
	p 6		8	14	75.0	42.9	6	19	25	31.6	24.0	9	45	54	20.0	16.7	-7	73	66	9.6	10.6
	t 12		49	61	24.5	19.7	20	53	73	37.7	27.4	21	80	101	26.3	20.8	-7	123	116	5.7	6.0
Cr	d 4		76	80	5.3	5.0	-27	336	363	8.0	7.4	17	78	95	21.8	17.9	-9	109	100	9.1	9.0
	p 262		1118	1380	23.4	19.0	-	-	-	-	-	951	6894	7845	13.8	12.1	641	7037	7678	9.1	8.4
	t 266		1194	1460	22.3	18.2	-	-	-	-	-	968	6972	7940	13.9	12.2	632	7146	7778	8.8	8.1
As	d 20		888	908	2.3	2.2	19	1794	1813	1.1	1.1	142	1412	1554	10.1	9.1	144	1007	1151	14.3	12.5
	p 186		421	607	44.2	30.6	-	-	-	-	-	-22	2013	1991	1.1	1.1	403	2638	3041	15.3	13.3
	t 206		1309	1515	15.7	13.6	-	-	-	-	-	120	3425	3545	3.5	3.4	547	3645	4192	15.0	13.0
Hg	d		Contaminated				-	-	-	-	-	2	14	12	14.3	16.7	Contaminated				
	p -1		43	42	2.2	2.4	23	157	180	14.7	12.8	21	137	158	15.3	13.3	23	198	221	11.6	10.4
	t		-	-	-	-	-	-	-	-	-	19	151	170	12.6	11.2	-	-	-	-	-
Cu <sup>(2)</sup>	d 26		719	745	3.6	3.5	56	829	885	6.8	6.3	71	839	910	8.5	7.8	29	931	960	3.1	3.0
	p		Contaminated				224	2122	2346	10.6	9.6	-298	4972	4674	6.0	6.4	-364	6555	6191	5.6	5.9
	t		-	-	-	-	280	295	3231	9.5	8.7	-227	5811	5584	3.9	4.1	-335	7486	7151	4.5	4.7

(1) Tidal cycle defined as that period of time during which the net transport of water is equal to the freshwater input to the estuary. Transport seawards is positive; landwards is negative.

(2) Stability of copper samples poor with respect to suspended solids - water interchange. Therefore, total copper is a more meaningful quantity.

that of Cu was seawards. No significant net transport of Cu was observed. Seaward transport dominated both the dissolved and particulate phases of the other elements, so tending to purge the estuary. Only in rare instances were landward transports seen, e.g. for dissolved Hg and particulate Cd, Ni.

#### ERRORS IN TRANSPORT DETERMINATIONS

##### *Contribution of individual errors to total*

A calculation of the total error in the net tidal transport of suspended solids is shown in Table 10. This incorporates

Table 9. Directions of the significant net tidal transports

		Direction	
		Landward (No of occasions)	Seaward (No of occasions)
Hg	d	1	0
	p	0	3
	t	0	1
As	d	0	2
	p	0	2
	t	0	2
Cr	d	0	1
	p	0	2
	t	0	2
Cd	d	0	3
	p	1	3
	t	0	3
Zn	d	0	0
	p	0	2
	t	0	2
Pb	d	0	3
	p	0	1
	t	0	2
Ni	d	0	1
	p	1	2
	t	0	1
Cu	t	0	0

realistic errors into each component measurement (concentration, velocity, lateral position, vertical position). This example, based on the 5.35 m tide survey, uses known analytical and current meter errors; the vertical and lateral position errors are judged subjectively. The total error in this case was calculated to be  $\pm 43.0\%$  (2 s.d.) and the largest contributor to this error was that of vertical position

( $\pm 35.8\%$ ). The vertical position error takes into account longitudinal shifts in the positions of the vessels and the resulting change in cross-sectional profile.

One potential source of error not included in these results is that arising from variability in velocity and concentration patterns which occurs between the anchored stations and which is ignored when the linear interpolation procedure is employed to calculate the fluxes. This concern was allayed eventually by a closely-spread rapid-drop profiling exercise, for suspended solids only, during the 1984 survey. Potter (1985) analysed these data and found that there was no significant difference between interpolated and RDP sample values.

##### *Error in net tidal transport in relation to the proportion of the half-tide transport*

Table 11 gives examples of errors calculated for some important determinands, using data from three of the tidal surveys. Viewed as a proportion of net tidal transport, the errors seem rather gross (ranging from 20 to 362% in column 7 of the table). However, it is more important to note the percentage errors in columns 8 and 9 where the proportion to half-tide transport is shown. Except for Cd (d) the latter errors are all of the order 4 to 6%, so that net/flood and net/ebb ratios exceeding 10% are significant, only eliminating the first line where the ratios are less than 2%. Even for Cd (d) the net/flood ratio is significantly above the 24% error estimate.

#### CROSS-SECTIONAL DISTRIBUTION OF METAL FLUXES

Discussion so far has dwelled solely on the integrated values of material transported in a tidal cycle. It is useful also to inspect the variation in fluxes across the survey section, at various phases of the tide. For the 7.22 m tidal range survey on 21.09.83 the 15 diagrams in Fig. 5 demonstrate the progressive variation in suspended solids throughout the low water/high water/low water tidal cycle. Starting from low water, there is the classic toe-in of sea water at depth, which then spreads to become a full flood tide with its maximum flux concentration near the right bank. This is not precisely reversed in the ebb, which at its height exhibits a much more symmetrical distribution of flux, such as at four hours after high water. For the 8.14 m tidal range survey on 16 September 1982, there was a particularly vigorous flux of particulate matter, strong flowing. Figure 6 shows some time frames of the particulate Hg fluxes for this event, again showing flux maxima at the right bank. For all four surveys a fairly intense core of high flux develops, extending across only a quarter of the estuary section, carrying the main burden

Table 10. Error in net tidal transport. Contribution to total error of errors in constituent measurements (16 June 1982 suspended solids data)

Assumed measurement error (one standard deviation)							Error in net tidal transport (2 s.d.)
Concentration		Velocity			Position (m)		
		Speed (m s <sup>-1</sup> )		Direction (deg)			
		Absolute (mg/l)	Percentage (%)		Absolute	Percentage (%)	
3	5	0.05	5	5	25	1	43.0
3	5	0	0	0	0	0	26.8
0	0	0.05	5	5	0	0	11.8
0	0	0	0	0	25	0	22.6
0	0	0	0	0	0	1	35.8

Table 11. Net tidal transport error in relation to the proportion of the half-tide transport

	TRANSPORT		ERROR (2 s.d.)					
	Mean	Net	Net/ Flood Ebb (%) (%)		In net	% of	% of half-tide	
	tidal	tidal			Net/	tidal	Net tidal	transport
	tange				transport	transport	Flood	Ebb
	(m)	(kg)			(kg)			
Susp. solids	6.17	$-423 \times 10^3$	1.6	1.7	$1530 \times 10^3$	362	6	6
As (d)	7.22	142	10.1	9.1	61	43	4	4
Susp. solids	5.35	$837 \times 10^3$	13.8	12.1	$360 \times 10^3$	43	6	5
Pb (p)	5.35	402	31.8	24.1	80	20	6	5
Cd (d)	6.17	14	41.2	29.2	8	52	24	17

of suspended matter. From such detailed information, which is also available for dissolved metal fluxes, stemmed the subsequent investigation by the Proudman Oceanographic Laboratory at Bidston into the relationship between metals flux at any one station and that across the whole cross-section, which will be reported separately.

#### NET TRANSPORT RESULTS VERSUS TIDAL RANGE

##### Total, dissolved and particulate results for each element

If a significant net total transport of an element occurred in any of the surveys, it implied a net movement in the seaward direction (Table 9). In this table the rather severe criterion was adopted, that a result had significance if the net/flood tide values  $>10\%$ . For the individual totals of As, Cd, Cr, Pb and Zn seaward net movement was thus found in more than one survey, but for Hg and Ni only one survey yielded a significant figure, also seaward. Total Cu did not produce a

definite result in terms of net transport for any of the four surveys. The transported masses of Cd, Ni, Pb and Zn tend to diminish with increase in tidal range (Table 8). It seems likely that tides generate a net seaward movement of these elements but during spring tides a landward component occurs. Figure 7 presents the data graphically and allows for the differing significance of individual results. Although not showing such a significant level as Ni, Pb, Zn and Cd, the same trend with range of tide appears for Cu. For Hg, As and Cr no clear trend could be identified.

##### Dissolved phase and particulate phase of each element

The half-tide transports of Cr, Pb, Zn and Hg were dominated by their particulate phases. There was a more even balance between dissolved and particulate matter for As, Cd and Ni. Trends of dissolved masses transported versus tidal range are not readily identified. Practically every dissolved case

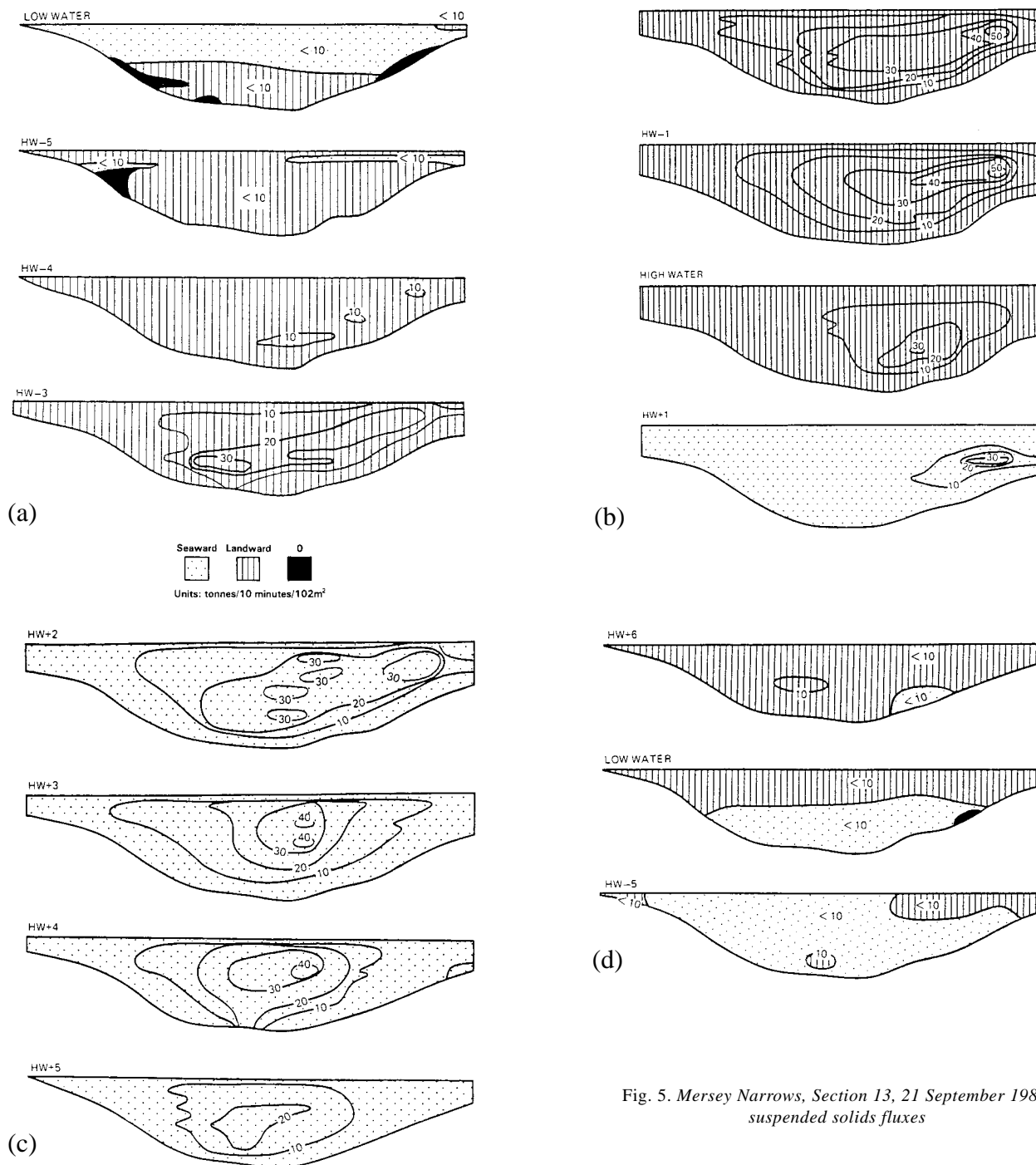


Fig. 5. Mersey Narrows, Section 13, 21 September 1983, suspended solids fluxes

shows a seawards transport. This is consistent with river flow, flushing out the estuary's former accumulation of metals. The particulate phase is consistent as regards direction of transport with behaviour of the total elements, as discussed above; this is not only true of elements like Cr, Pb and Zn, whose particulate phase predominates, but for the others also. Only As shows an apparent anomaly in the 7.22 m tide, but the figure is non-significant.

#### *Dissolved metal concentrations and their EQS values*

A comparison between the concentration ranges of dissolved metals observed during the four surveys and their respective recommended EQS values (Mance, 1984) is presented in Table 12. Only in the cases of Cu, Zn and Pb were the EQS values exceeded, although it should be remembered that the latter refer to "annual average values". Furthermore, in each of these three cases the number of samples in which the EQS was exceeded was small compared with the total number of samples collected during each survey (approximately 300).

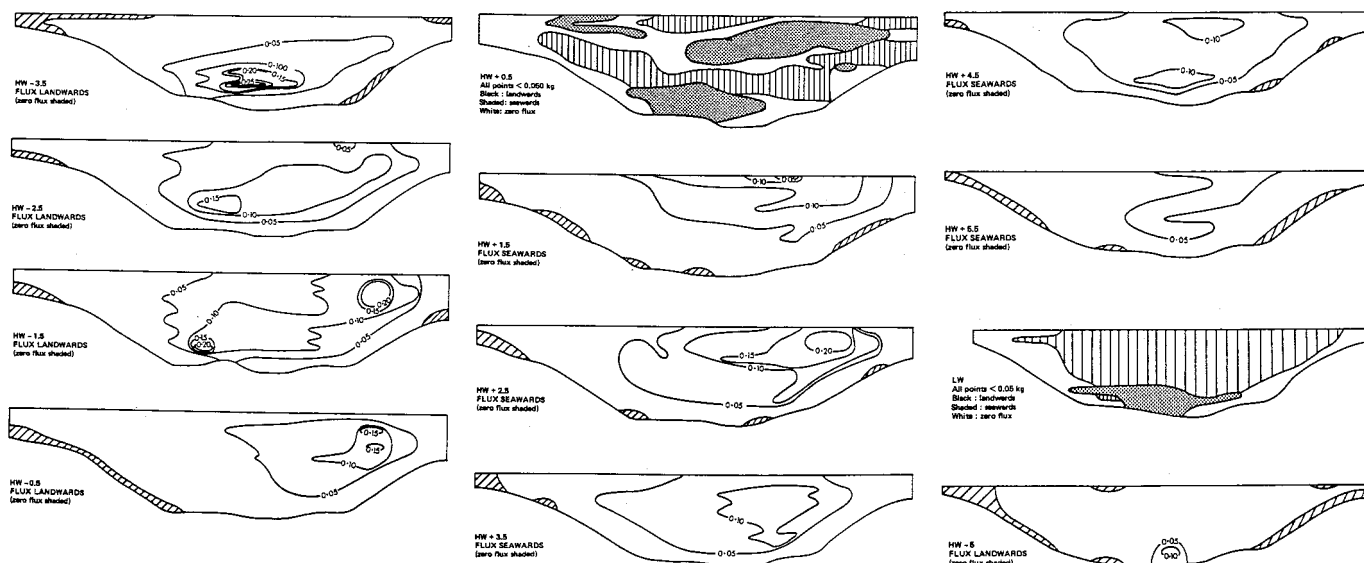


Fig. 6. Mersey Narrows, Section 13, Spring tide (16 September 1982) — spatial and temporal variation of particulate Hg fluxes (contours at 0.050 kg intervals, except where indicated otherwise).

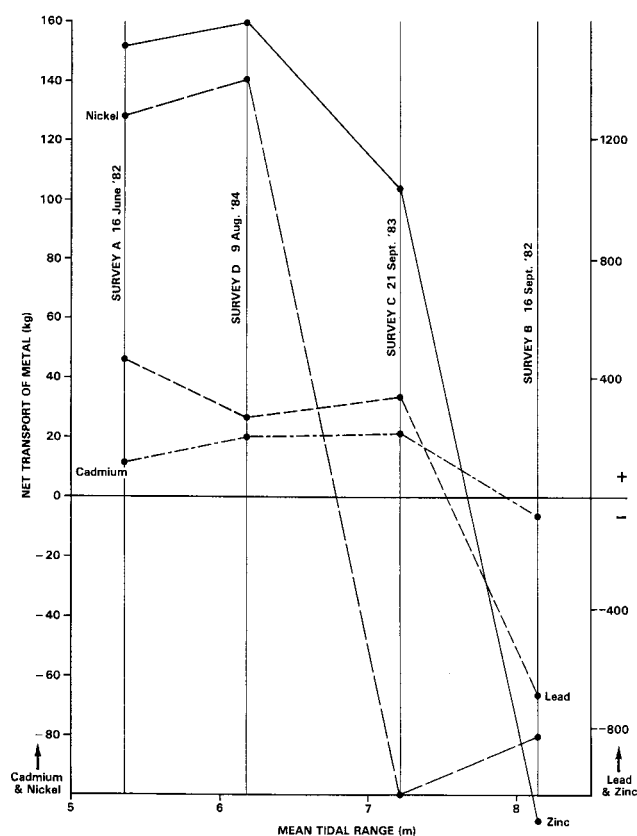


Fig. 7. Net transport of metal versus tidal range

## Summary and conclusions

### INTENSIVE DATA ACQUIRED ACROSS THE MERSEY NARROWS

The four cross-sectional tidal-cycle surveys in the Mersey Narrows entailed a major logistic organisation of boats and scientists out in the estuary for each survey, together with a major chemical analytical effort by laboratory staff. Each survey generated over 300 samples which were filtered and sub-sampled for measuring As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in their dissolved and particulate phases, yielding over 4800 determinations per survey. For most of the metals, the particulate phase was dominant; the exception was Cd, for which the dissolved and particulate concentrations were similar.

Each tidal-cycle survey incorporated current meter measurements at 26 points in the cross-section every half hour, together with frequent vertical profiles of salinity and turbidity; this work was mainly tackled by Hydraulics Research Ltd. Surveyors were also contracted in to give fixes on all the survey vessels which had received special permission to anchor in the Narrows from the Mersey Docks and Harbour Company.

### SIGNIFICANT RESULTS FROM THE TIDAL CYCLE SURVEYS

Net tidal transports from the Mersey estuary to the nearby coastal zone (and vice versa) have been derived from the

Table 12. Comparison of concentration ranges of dissolved metals and their respective EQS values

	Mean tidal range (m)						Recommended EQS			
	5.35		6.17		7.22		8.14		(annual average) (mg l <sup>-1</sup> )	
	Concentration		Concentration		Concentration		Concentration			
	Min	Max	Min	Max	Min	Max	Min	Max		
Cr	0.06	1.7	0.6	12.7	0.03	0.81	0.16	0.91	15	
As	1.9	6.5	3.2	10.2	1.1	10.9	1.5	7.4	25	
Ni	2.0	13.3	1.47	6.56	1.0	5.85	1.11	10.8	30	
Cu <sup>f</sup>	2.3	13.3	0.20	11.3	2.2	7.25	2.26	6.4	[5]	
Zn <sup>g</sup>	10.44	42.75	8.58	50.0	24.7	48.3	12.3	44.1	40	
Cd	0.10	1.66	0.06	0.93	0.07	0.41	0.08	0.33	5	
Pb <sup>h</sup>	1.1	6.9	0.31	53.1	0.13	6.35	0.46	4.72	25	
(inorg)										
Hg*	Contaminated		11.5	166.3	0.5	75.4	Contaminated		500	

\* concentration units ng l<sup>-1</sup>

[ ] higher values acceptable where acclimation expected or if copper is present in organic complexes

<sup>f</sup> No. of samples > EQS	<sup>g</sup> No. of samples > EQS	<sup>h</sup> No. of samples > EQS
5.35 7	5.35 1	6.17 1
6.17 5	6.17 2	
7.22 2	7.22 3	
8.14 4	8.14 5	

hour-by-hour flux data from each of the four tidal-cycle surveys. In terms of the mass transported, Zn was the dominant metal, with over 30 tonnes being moved seawards on spring ebb tides and similar amounts landwards on spring flood tides. The mass transports of As, Cu, Cr and Pb were about a third those of Zn. Those of Ni were about one tenth, and those of Cd and Hg yet less, but still in amounts of environmental concern. From the difference between the ebb and flood transports, and allowing for the freshwater flow on each occasion, the net transport seawards of each component was arrived at. These calculated net transports are shown to be significant when they are greater or equal to 10% of the half-tide transport. The largest contribution to the total error in a net tidal transport was that derived from a longitudinal shift in the position of a sampling station during a survey. Any further error due to the use of a linear interpolation procedure, to account for the concentration and velocity gradients which exist between stations at any given time, is seen as minor compared to the other imperfections of measurement.

A landward net tidal transport was observed only for certain of the elements under investigation when there were

large-amplitude tides running. Such spring tides did produce some apparent landward movement of Cd, Ni, Pb and Zn, if some figures ~5% of half-tide transport are admissible. On the other hand, significant seaward transports were seen on more than one occasion in the cases of Cr, Cd, As, Zn and Pb and on one occasion for each of Hg and Ni. Cu did not exhibit a significant net tidal transport during any of the four surveys. The half-tide transports of Cr, Pb and Hg were dominated by the particulate phase, whereas both the latter and the dissolved phase were important for As, Cd and Ni. Significant landward net tidal transports were observed only for dissolved Hg and particulate Cd and Ni, in each case on one occasion only. On the other hand, significant seaward net tidal transports were observed for both the particulate and dissolved phases of all elements, on one or more occasions in each case, the exceptions being dissolved Zn and Hg. Recommended Environmental Quality Standard values for dissolved metals were met in all cases. For most of the metals, concentrations were consistently below the standard values (annual averages), although on a few occasions higher concentrations of Zn, Cu and Pb were recorded.



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